

FORM PTO-1300 (REV. 11-2000)		U.S. DEPARTMENT OF COMMERCE PATENT AND TRADEMARK OFFICE		ATTORNEY'S DOCKET NUMBER	
TRANSMITTAL LETTER TO THE UNITED STATES DESIGNATED/ELECTED OFFICE (DO/EO/US) CONCERNING A FILING UNDER 35 U.S.C. 371				MCA-464	
				U.S. APPLICATION NO. (If known, see 37 CFR 1.5)	
				10/009744	
INTERNATIONAL APPLICATION NO. PCT/US00/14976		INTERNATIONAL FILING DATE 31 May 2000		PRIORITY DATE CLAIMED 4 June 1999	
TITLE OF INVENTION HYDROPHOBIC AND HYDROPHILIC MEMBRANES TO VENT TRAPPED GASES IN A PLATING CELL APPLICANT(S) FOR DO/EO/US					
David W. Stockbower					
Applicant herewith submits to the United States Designated/Elected Office (DO/EO/US) the following items and other information:					
<p>1. <input checked="" type="checkbox"/> This is a <b>FIRST</b> submission of items concerning a filing under 35 U.S.C. 371.</p> <p>2. <input type="checkbox"/> This is a <b>SECOND</b> or <b>SUBSEQUENT</b> submission of items concerning a filing under 35 U.S.C. 371.</p> <p>3. <input checked="" type="checkbox"/> This is an express request to begin national examination procedures (35 U.S.C. 371(f)). The submission must include items (5), (6), (9) and (21) indicated below.</p> <p>4. <input checked="" type="checkbox"/> The US has been elected by the expiration of 19 months from the priority date (Article 31).</p> <p>5. <input checked="" type="checkbox"/> A copy of the International Application as filed (35 U.S.C. 371(c)(2))</p> <p style="margin-left: 20px;">a. <input type="checkbox"/> is attached hereto (required only if not communicated by the International Bureau).</p> <p style="margin-left: 20px;">b. <input type="checkbox"/> has been communicated by the International Bureau.</p> <p style="margin-left: 20px;">c. <input checked="" type="checkbox"/> is not required, as the application was filed in the United States Receiving Office (RO/US).</p> <p>6. <input type="checkbox"/> An English language translation of the International Application as filed (35 U.S.C. 371(c)(2)).</p> <p style="margin-left: 20px;">a. <input type="checkbox"/> is attached hereto.</p> <p style="margin-left: 20px;">b. <input type="checkbox"/> has been previously submitted under 35 U.S.C. 154(d)(4).</p> <p>7. <input checked="" type="checkbox"/> Amendments to the claims of the International Application under PCT Article 19 (35 U.S.C. 371(c)(3))</p> <p style="margin-left: 20px;">a. <input type="checkbox"/> are attached hereto (required only if not communicated by the International Bureau).</p> <p style="margin-left: 20px;">b. <input type="checkbox"/> have been communicated by the International Bureau.</p> <p style="margin-left: 20px;">c. <input type="checkbox"/> have not been made; however, the time limit for making such amendments has NOT expired.</p> <p style="margin-left: 20px;">d. <input checked="" type="checkbox"/> have not been made and will not be made.</p> <p>8. <input type="checkbox"/> An English language translation of the amendments to the claims under PCT Article 19 (35 U.S.C. 371 (c)(3)).</p> <p>9. <input type="checkbox"/> An oath or declaration of the inventor(s) (35 U.S.C. 371(c)(4)).</p> <p>10. <input type="checkbox"/> An English language translation of the annexes of the International Preliminary Examination Report under PCT Article 36 (35 U.S.C. 371(c)(5)).</p> <p>Items 11 to 20 below concern document(s) or information included:</p> <p>11. <input type="checkbox"/> An Information Disclosure Statement under 37 CFR 1.97 and 1.98.</p> <p>12. <input type="checkbox"/> An assignment document for recording. A separate cover sheet in compliance with 37 CFR 3.28 and 3.31 is included.</p> <p>13. <input type="checkbox"/> A FIRST preliminary amendment.</p> <p>14. <input type="checkbox"/> A SECOND or SUBSEQUENT preliminary amendment.</p> <p>15. <input type="checkbox"/> A substitute specification.</p> <p>16. <input type="checkbox"/> A change of power of attorney and/or address letter.</p> <p>17. <input type="checkbox"/> A computer-readable form of the sequence listing in accordance with PCT Rule 13ter.2 and 35 U.S.C. 1.821 - 1.825.</p> <p>18. <input type="checkbox"/> A second copy of the published international application under 35 U.S.C. 154(d)(4).</p> <p>19. <input type="checkbox"/> A second copy of the English language translation of the international application under 35 U.S.C. 154(d)(4).</p> <p>20. <input checked="" type="checkbox"/> Other items or information:</p> <p style="margin-left: 20px;">1. Copy of the International Preliminary Examination Report;</p> <p style="margin-left: 20px;">2. Copy of the International Search Report; and</p> <p style="margin-left: 20px;">3. Copy of Form PCT/IB/308.</p>					

U.S. APPLICATION NO. <u>10000001</u> 37 CFR 1.52		INTERNATIONAL APPLICATION NO. <u>PCT/US00/14976</u>		ATTORNEY'S DOCKET NUMBER <u>MCA-464</u>	
21. <input checked="" type="checkbox"/> The following fees are submitted: <b>BASIC NATIONAL FEE (37 CFR 1.492 (a) (1) - (5)):</b> Neither international preliminary examination fee (37 CFR 1.482) nor international search fee (37 CFR 1.445(a)(2)) paid to USPTO and International Search Report not prepared by the EPO or JPO ..... \$10*0.00 International preliminary examination fee (37 CFR 1.482) not paid to USPTO but International Search Report prepared by the EPO or JPO ..... \$890.00 International preliminary examination fee (37 CFR 1.482) not paid to USPTO but international search fee (37 CFR 1.445(a)(2)) paid to USPTO ..... \$7*0.00 International preliminary examination fee (37 CFR 1.482) paid to USPTO but all claims did not satisfy provisions of PCT Article 33(1)-(4) ..... \$7*0.00 International preliminary examination fee (37 CFR 1.482) paid to USPTO and all claims satisfied provisions of PCT Article 33(1)-(4) ..... \$100.00 <b>ENTER APPROPRIATE BASIC FEE AMOUNT =</b>				<b>CALCULATIONS PTO USE ONLY</b>	
Surcharge of \$130.00 for furnishing the oath or declaration later than months from the earliest claimed priority date (37 CFR 1.492(e)). <input type="checkbox"/> 20 <input checked="" type="checkbox"/> 30				\$ 100.00	
				\$ 130.00	
<b>CLAIMS</b>	<b>NUMBER FILED</b>	<b>NUMBER EXTRA</b>	<b>RATE</b>	<b>\$</b>	
Total claims	10 - 20 =	0	x \$18.00	\$ 0	
Independent claims	4 - 3 =	1	x \$8*0.00	\$ 84.00	
MULTIPLE DEPENDENT CLAIM(S) (if applicable)			+ \$280.00	\$ 0	
<b>TOTAL OF ABOVE CALCULATIONS =</b>				\$ 314.00	
<input type="checkbox"/> Applicant claims small entity status. See 37 CFR 1.27. The fees indicated above are reduced by 1/2.					
<b>SUBTOTAL =</b>				\$ 314.00	
Processing fee of \$130.00 for furnishing the English translation later than months from the earliest claimed priority date (37 CFR 1.492(f)). <input type="checkbox"/> 20 <input type="checkbox"/> 30					
<b>TOTAL NATIONAL FEE =</b>				\$ 314.00	
Fee for recording the enclosed assignment (37 CFR 1.21(h)). The assignment must be accompanied by an appropriate cover sheet (37 CFR 3.28, 3.31). \$40.00 per property +				\$ 0	
<b>TOTAL FEES ENCLOSED =</b>				\$ 314.00	
				Amount to be refunded:	\$
				charged:	\$
a. <input checked="" type="checkbox"/> A check in the amount of \$ <u>314.00</u> to cover the above fees is enclosed. b. <input type="checkbox"/> Please charge my Deposit Account No. _____ in the amount of \$ _____ to cover the above fees. A duplicate copy of this sheet is enclosed. c. <input checked="" type="checkbox"/> The Commissioner is hereby authorized to charge any additional fees which may be required, or credit any overpayment to Deposit Account No. <u>14-0930</u> . A duplicate copy of this sheet is enclosed. d. <input type="checkbox"/> Fees are to be charged to a credit card. <b>WARNING:</b> Information on this form may become public. Credit card information should not be included on this form. Provide credit card information and authorization on PTO-2038.					
<b>NOTE: Where an appropriate time limit under 37 CFR 1.494 or 1.495 has not been met, a petition to revive (37 CFR          1.137 (a) or (b)) must be filed and granted to restore the application to pending status.</b>					
SEND ALL CORRESPONDENCE TO:					
Kevin S. Lemack Nields & Lemack 176 E. Main Street Westboro, MA 01581					
SIGNATURE _____ Kevin S. Lemack NAME _____ 32,579 REGISTRATION NUMBER _____					

HYDROPHOBIC AND HYDROPHILIC MEMBRANES TO VENT  
TRAPPED GASES IN A PLATING CELL

BACKGROUND OF THE INVENTION

5 In semiconductor manufacturing, a plating tool uses  
a negatively charged anode (usually a copper anode) to plate  
a positively charged (cathode) silicon wafer. The anode  
provides a source of replenishing metal ions. At the cathode,  
the metal ions are reduced to metal and deposited on the  
10 cathode surface. Sulfuric acid and a plating solution flows  
through a chamber around the anode and is used to dissolve a  
metal (copper) plate. As fluid flows past the anode, it  
becomes enriched with metal ions.

15 During the chemical reaction that dissolves the metal  
(e.g., copper), hydrogen gas is liberated. In addition,  
entrapped gases are generally present during start-up. These  
gases must be vented so that they do not effect the electrical  
field or the wafer plating uniformity. Indeed, a separate  
upstream degasser removes most dissolved air from the main  
20 fluid flow path. The generated hydrogen gas, if not removed,  
becomes entrapped in the plating solution as bubbles or  
microbubbles and may interfere with the plating operation.

25 It therefore would be desirable to provide a means for  
venting hydrogen gas and any other trapped gases out of the  
plating solution before the solution reaches the wafer.

SUMMARY OF THE INVENTION

30 The problems of the prior art have been overcome by the  
present invention, which provides a plating anode cup filter  
design that vents unwanted gases from the plating solution  
before they exit the cell and reach the wafer. More  
specifically, in a first embodiment of the present invention,  
in the chamber where the fluid flows into the plating tool cell  
and contacts the anode, it encounters a hydrophobic membrane  
35 and a hydrophilic membrane spaced from the hydrophobic  
membrane. A driving force such as a vacuum applied in the  
space between the membranes removes unwanted gases therein.

In a second embodiment of the present invention, a single membrane is used that is both hydrophobic and hydrophilic. Preferably the hydrophobic portion of the membrane is located at or near the perimeter of the fluid chamber in the plating tool cell, and gas to be vented is directed toward the hydrophobic portion(s).

#### BRIEF DESCRIPTION OF THE DRAWINGS

Figure 1 is a cross-sectional view of the anode holder in accordance with the present invention;

Figure 2 is a cross-sectional view of the anode holder in accordance with another embodiment of the present invention;

Figure 3 is a top view of a membrane having hydrophilic and a hydrophobic portions in accordance with one embodiment of the present invention;

Figure 4 is a cross-sectional view of an anode holder using the membrane of Figure 3; and

Figure 5 is a cross-sectional view of still another embodiment of the present invention.

#### DETAILED DESCRIPTION OF THE INVENTION

Turning now to Figure 1, there is shown an anode for use in semiconductor manufacturing. A plating tool cell 10 is the housing for the anode 50, which is preferably a copper anode, and includes one or more fluid inlets 12. Thus, the plating tool cell 10 serves as an anode holder and as a means for fluid distribution to the substrate being plated, such as a wafer (not shown) which is typically rotating for uniform plating. Preferably the plating tool cell 10 is made of plastic, and includes an optional fluid inlet 12 and a fluid outlet 13.

A fluid plating solution or ion source, such as copper sulfate, is introduced into a chamber defined by the plating tool cell 10 through optional fluid inlet 12, and contacts the anode 50. The resulting reaction between the plating solution and the metal anode generates hydrogen gas. In the embodiment shown, situated in the fluid path is a hydrophobic membrane 14. The hydrophobicity of the membrane 14 inhibits or prevents

5 passage of the fluid. However, the porosity of the hydrophobic membrane 14 is such that gases, generally air and hydrogen, entrapped in the fluid are able to pass through the hydrophobic membrane 14 easily. A second membrane 15 is positioned downstream of the first membrane (in the direction away from the anode 50). The second membrane 15 is spaced from the first membrane 14, and is hydrophilic. Once the hydrophilic membrane 15 is wetted, it does not allow the passage of gases through it. Accordingly, most or all of the gases remain in the gap 16 between the two membranes. The gap 16 can be filled with a open mesh type separation material, and may be 1/16 to 1/4 inch wide, on average. A driving force such as a vacuum source in communication with the gap 16 with suitable plumbing draws off the gases, thereby preventing them from contacting the wafer and causing defects. Alternatively, high velocity air can be used to create a vacuum by the venturi effect to draw off the gases. Figure 2 shows another embodiment where the gases are vented in gap 16 by creating a high spot 23 in the gap 16 mechanically. The high spot 23 is a portion of the gap 16 that is wider, from membrane 14 to membrane 15, than the total average width of the gap 16. The air tends to collect in the high spot 23 and vent naturally, or can be assisted with a vacuum or high velocity air pressure. The high spot 23 also can be created by bowing the membrane with external fluid pressure, leaving high spots during processing.

Figure 3 illustrates another embodiment of the present invention. In this embodiment, the membrane 14' is patterned such that only a portion 28 thereof is hydrophobic. Conventional techniques to render portions of the membrane hydrophobic well known to those skilled in the art can be used. Preferably, the hydrophobic portion(s) are located at or near the perimeter of the cell 10, and the fluid flow is directed towards the perimeter, as shown in Figure 4.

Figure 5 illustrates another embodiment of the present invention, where a high spot 23 is created and a small hydrophobic membrane patch 15' is used in a vertical orientation. The hydrophobic membrane 15 is optional, and a

bowed hydrophilic membrane 14 is positioned to create a high spot 23 as in the embodiment of Figure 2. The air trapped in gap 16 vents naturally through hydrophobic patch 15' without the use of an external driving force such as a vacuum.

5

The removal of bubbles from the plating solution prior to their reaching the wafer contributes to lower plating defects on the wafer.

What is claimed is:

1. An anode plating cell, comprising:

an anode;

5 a housing for said anode, said housing having a fluid inlet and a fluid outlet;

a hydrophobic membrane in said housing downstream of said anode;

10 a hydrophilic membrane in said housing downstream of and spaced from said hydrophobic membrane by a gap;

whereby gases entrapped in said fluid pass through said hydrophobic membrane into said gap and are prevented from passing through said hydrophilic membrane.

2. The anode plating cell of claim 1, further comprising a driving force for removing said entrapped gases from said gap.

3. The anode plating cell of claim 2, wherein said driving force is a vacuum.

4. The anode plating cell of claim 1, wherein said anode comprises copper.

20 5. An anode plating cell, comprising:

an anode;

a housing for said anode, said housing having a fluid inlet and a fluid outlet;

25 a membrane in said housing downstream of said anode, said membrane having a hydrophobic portion permeable to said fluid and to gases entrapped in said fluid, and a hydrophilic portion permeable to said fluid but not to said gases.

30 6. The anode plating cell of claim 5, further comprising a driving force for removing said entrapped gases from said housing.

7. The anode plating cell of claim 6, wherein said driving force is a vacuum.

8. The anode plating cell of claim 5, wherein said anode comprises copper.

35 9. A method of removing gases entrapped in a plating solution from an anode plating cell, comprising:  
providing an anode in said cell;

providing a hydrophobic membrane in said cell downstream of said anode;

providing a hydrophilic membrane in said cell spaced from and downstream of said hydrophobic membrane;

circulating plating solution in said anode plating cell to contact said plating solution with said anode;

causing gases entrapped in said plating solution to pass through said hydrophobic membrane but not through said hydrophilic membrane; and

removing said gases from said cell.

10. A method of removing gases entrapped in a plating solution from an anode plating cell, comprising:

providing an anode in said cell;

circulating a plating solution in said cell;

causing said plating solution to contact said anode;

providing a membrane in said cell downstream of said anode, said membrane having a hydrophobic portion permeable to said plating solution and to entrapped gases in said plating solution, and a hydrophilic portion permeable to said plating solution but not to gases entrapped in said plating solution;

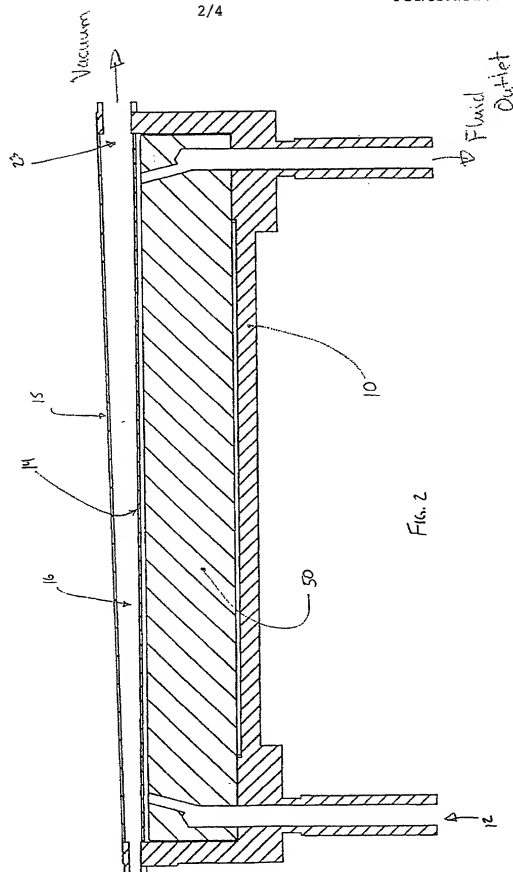
causing gases entrapped in said plating solution to pass through said hydrophobic portion of said membrane but not through said hydrophilic portion; and

removing said gases from said cell.





FIG. 2



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Fig. 3

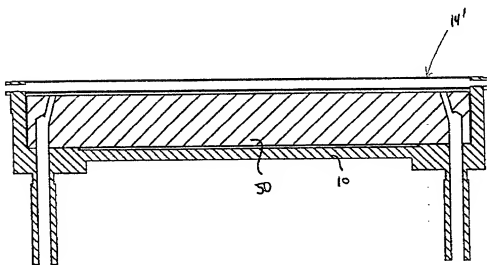
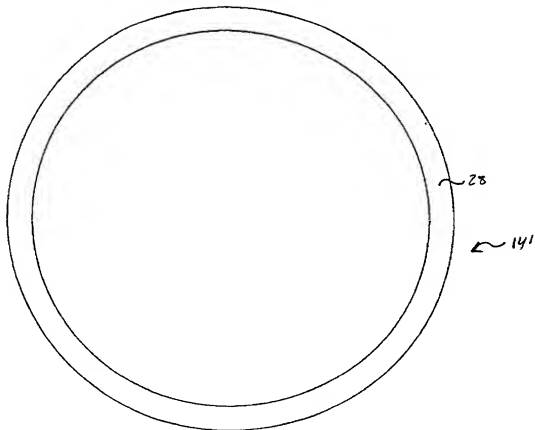
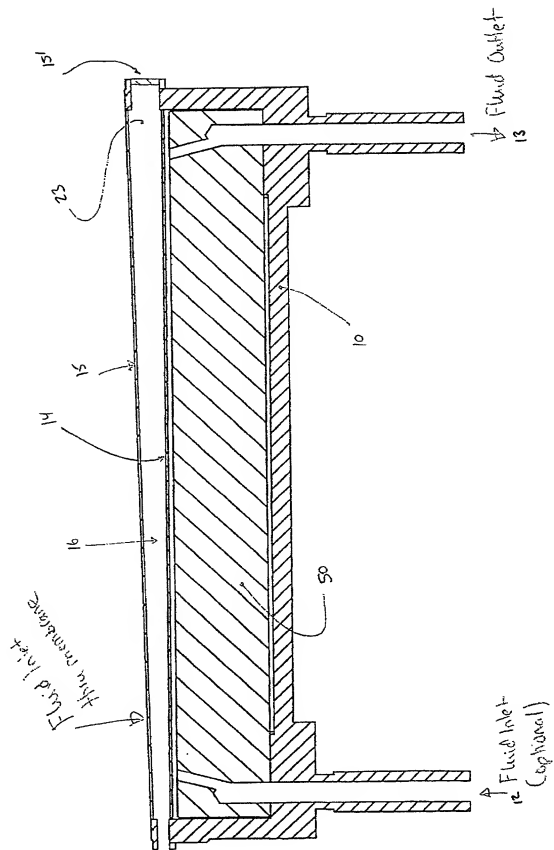


Fig. 4

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PTO/SB/01 (10-00)

Approved for use through 10/31/2002. OMB 0651-0032

U.S. Patent and Trademark Office; U.S. DEPARTMENT OF COMMERCE

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# **DECLARATION FOR UTILITY OR DESIGN PATENT APPLICATION (37 CFR 1.63)**

☐ Declaration Submitted with Initial Filing      OR      ☒ Declaration Submitted after Initial Filing (surcharge (37 CFR 1.16 (e)) required)

Attorney Docket Number	MCA-464
First Named Inventor	David W. Stockbower
<b>COMPLETE IF KNOWN</b>	
Application Number	10 / 009,744
Filing Date	December 4, 2001
Group Art Unit	
Examiner Name	

As a below named inventor, I hereby declare that:

My residence, mailing address, and citizenship are as stated below next to my name.

I believe I am the original, first and sole inventor (if only one name is listed below) or an original, first and joint inventor (if plural names are listed below) of the subject matter which is claimed and for which a patent is sought on the invention entitled:

HYDROPHOBIC AND HYDROPHILIC MEMBRANES TO VENT  
TRAPPED GASES IN A PLATING CELL

(Title of the Invention)

the specification of which

☐ is attached hereto

OR

☒ was filed on (MM/DD/YYYY) May 31, 2000 as United States Application Number or PCT International

Application Number PCT/US00/14976 and was amended on (MM/DD/YYYY) (if applicable).

I hereby state that I have reviewed and understand the contents of the above identified specification, including the claims, as amended by any amendment specifically referred to above.

I acknowledge the duty to disclose information which is material to patentability as defined in 37 CFR 1.56, including for continuation-in-part applications, material information which became available between the filing date of the prior application and the national or PCT international filing date of the continuation-in-part application.

I hereby claim foreign priority benefits under 35 U.S.C. 119(a)-(d) or 365(b) of any foreign application(s) for patent or inventor's certificate, or 365(a) of any PCT international application which designated at least one country other than the United States of America, listed below and have also identified below, by checking the box, any foreign application for patent or inventor's certificate, or any PCT international application having a filing date before that of the application on which priority is claimed.

Prior Foreign Application Number(s)	Country	Foreign Filing Date (MM/DD/YYYY)	Priority Not Claimed	Certified Copy Attached? YES NO
			<input type="checkbox"/> <input type="checkbox"/> <input type="checkbox"/> <input type="checkbox"/>	<input type="checkbox"/> <input type="checkbox"/> <input type="checkbox"/> <input type="checkbox"/>

☐ Additional foreign application numbers are listed on a supplemental priority data sheet PTO/SB/02B attached hereto:

I hereby claim the benefit under 35 U.S.C. 119(e) of any United States provisional application(s) listed below.

Application Number(s)	Filing Date (MM/DD/YYYY)	<input type="checkbox"/> Additional provisional application numbers are listed on a supplemental priority data sheet PTO/SB/02B attached hereto.
60/137,558	June 4, 1999	

[Page 1 of 2]

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PTO/SB/81 (10-00)

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## POWER OF ATTORNEY OR AUTHORIZATION OF AGENT

Application Number	10/009,744
Filing Date	December 4, 2001
First Named Inventor	David W. Stockbower
Group Art Unit	
Examiner Name	
Attorney Docket Number	MCA-464

I hereby appoint:

☐ Practitioners at Customer Number

Place Customer  
Number Bar Code  
Label here

OR

☒ Practitioner(s) named below:

Name	Registration Number
Kevin S. Lemack	32,579
Henry C. Nields	17,029

as my/our attorney(s) or agent(s) to prosecute the application identified above, and to transact all business in the United States Patent and Trademark Office connected therewith.

Please change the correspondence address for the above-identified application to:

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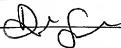
<input checked="" type="checkbox"/> Firm or Individual Name	Kevin S. Lemack				
Address	Nields & Lemack				
Address	176 E. Main Street				
City	Westboro	State	MA	Zip	01581
Country	U.S.A.				
Telephone	(508) 898-1818	Fax	(508) 898-2020		

I am the:

☒ Applicant/Inventor.

☐ Assignee of record of the entire interest. See 37 CFR 3.71.  
Statement under 37 CFR 3.73(b) is enclosed. (Form PTO/SB/96).

### SIGNATURE of Applicant or Assignee of Record

Name	David W. Stockbower
Signature	 4/18/02
Date	

NOTE: Signatures of all the inventors or assignees of record of the entire interest or their representative(s) are required. Submit multiple forms if more than one signature is required, see below.

☐ \*Total of \_\_\_\_\_ forms are submitted.

**DECLARATION — Utility or Design Patent Application**

Direct all correspondence to:

☐ Customer Number  
or Bar Code LabelOR ☒

Correspondence address below

Name Kevin S. LemackAddress Nields & LemackAddress 176 E. Main StreetCity WestboroState MAZIP 01581Country U.S.A.Telephone (508) 898-1818Fax (508) 898-2020

I hereby declare that all statements made herein of my own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under 18 U.S.C. 1001 and that such willful false statements may jeopardize the validity of the application or any patent issued thereon.

NAME OF SOLE OR FIRST INVENTOR: David W.☐ A petition has been filed for this unsigned inventorGiven Name  
(first and middle (if any)) David W.Family Name  
or Surname StockbowerInventor's  
Signature [Signature]Date 1/18/02Residence: City BurlingtonState MACountry USCitizenship USMailing Address 85 Center Street

Mailing Address

City BurlingtonState MAZIP 01803Country US

NAME OF SECOND INVENTOR:

☐ A petition has been filed for this unsigned inventorGiven Name  
(first and middle (if any))Family Name  
or SurnameInventor's  
Signature

Date

Residence: City

State

Country

Citizenship

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☐ Additional inventors are being named on the \_\_\_\_\_ supplemental Additional Inventor(s) sheet(s) PTO/SB/02A attached hereto.